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EUROPEAN PATENT APPLICATION

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(54) Single crystal silicon.

(57) Single crystal silicon for a substrate of semiconductor integrated circuits is disclosed. Cu, Fe, Ni and Cr are contained as impurities in a concentration smaller than 0.1 ppta, respectively, and the total content of the impurities is less than 0.4 ppta. Oxygen-induced stacking faults are reduced to an absolute minimum.

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Description

The present invention relates to single crystal silicon typically for use as a substrate of semiconductor integrated circuits. More particularly, the invention is directed to such single crystal silicon in which contamination with certain specific impurities is minimized in the bulk of the substrate so that stacking faults induced on main or front surfaces during thermal oxidation are reduced substantially to zero.

Thermal oxidation is commonly accepted as requisite of processing integrated circuits, particularly those of an MOS type. Oxygen-induced stacking faults referred to simply as OSF and developed while in treatment of single crystal silicon at elevated temperature are found significantly contributive to the electrical characteristics of the integrated circuit to be formed. OSF, therefore, has heretofore been a great concern in the electronics industry.

OSF is generally known to grow in an oxidative atmosphere and to reduce under a non-oxidative condition. This type of fault is reportedly attributable to (a) mechanical strains induced during wafer fabrication, (b) point defects developed and accumulated in heat processing, (c) defects due to ion implantation. (d) surface contaminations with Na, and (e) surface defects such as so-called swirl defects and bulk defects originating from dissolved oxygen deposition.

The surface and bulk defects among those factors are closely associated with various intrinsic gettering (IG) treatments effected initially in the production of integrated circuits from silicon wafers. The gettering effect induced in a silicon wafer is effective in preventing the wafer from getting involved in OSF as they are capable of rendering the wafer fully free from oxygen-induced minute defects at the active surface layer. It has been further proposed, as taught for instance by Japanese Patent Laid-open Publication No. 55-56098, that oxygen-induced bulk defects in the bulk of single crystal silicon be prohibited by controlling the thermal history of single crystal silicon during the period of time when the latter material is being pulled by Czochralski method. This prior process is intended to subject a rod of single crystal silicon just following the whole growth process in a temperature region of 900 to 500° C in the furnace chamber for not longer than 4 hours and thereafter at a cooling speed of not lower than 100° C per hour.

The surface and bulk defects would also be expected to result from contamination with metallic impurities. To this end, many attempts have been made to examine and detect those contaminants introduced in single crystal silicon, as disclosed in the following publications. However, none of them make a detailed analysis of the correlation between the individual metals and the OSF levels.

1. P. F. Schmit et al, "Solid-state Science and Technology", J. Electrochem. Soc., p.632 (1981)
2. Nakajima and Ohara, "Chemical Analyses of Semiconductors", Ohyô Butsuri, Vol. 43, No. 5, p.438 (1974)
3. Nakajima, Bando and Nakayama, "Neutron Activation Analyses of Impurities in Highly Pure Silicon Semiconductors", Bunseki Kiki, Vol. 6, No. 9, p572 (1968)
4. Shirai, "Pulling Technology of Single Crystal Silicons", Zairyo Gijutsu, Vol. 2, No. 1, p.41 (1984)

Neutron activation analysis allows a limited group of metals such as Au to be detected in the order of ppta (parts per 10^{12}) but fails to measure various other metals up to such level of concentration.

Under the above state of technologies, there has been left unsolved the technical problem of OSF being held at a substantially nil level in single crystal silicon.

The present invention seeks to provide single crystal silicon for use as a substrate of semiconductor integrated circuits which exhibits lesser susceptibility to OSF on a semiconducting substrate and has an OSF density of not more than 10 or 100 pieces/cm² for an n-type, (100)-orientation semiconducting substrate.

The single crystal silicon according to the present invention, because of its minimum generation of OSF, is favourably applicable to the production of various semiconductor devices of superior electrical characteristics.

According to one aspect of the invention, there is provided an n-type (100) oriented single crystal silicon for use as a substrate for semiconductor integrated circuits, which comprises as impurities Cu, Fe, Ni and Cr in an individual concentration of not more than 0.1×10^{-6} ppma and in a total concentration of not more than 0.4×10^{-6} ppma, whereby the silicon has not more than 100 oxygen-induced stacking faults per cm².

According to another aspect of the invention, there is provided an n-type (100) oriented single crystal silicon for use as a substrate for semiconductor integrated circuits, which comprises as impurities Cu, Fe, Ni, Cr, Ti and Mn in an individual concentration of not more than 0.1×10^{-6} ppma and in a total concentration of not more than 0.6×10^{-6} ppma, whereby the silicon has not more than 10 oxygen-induced stacking faults per cm².

Single crystal silicon according to the present invention is suitable for the production of various semiconductor devices of superior electrical characteristics. A first form of single crystal silicon contemplated under the invention comprises metallic contaminants in which are included Cu, Fe, Ni and Cr. Each of the contaminants should not be greater than 0.1×10^{-6} ppma in concentration, whereas all these contaminants should be smaller than 0.4×10^{-6} ppma in total content. By strict observance of these requirements, the OSF density is maintained at below 100 pieces/cm^2 as an n-type semiconductor substrate (100)-oriented and mirrorpolished.

A second form of silicon is so structured as to have an OSF density of less than 10 pieces/cm^2. In such instance, metallic impurities are Cu, Fe, Ni, Cr, Ti and Mn, respectively, in a concentration of not more than 0.1×10^{-6} ppma and, on the whole, in a content of not more than 0.6×10^{-6} ppma. To attain OSF densities up to 100 pieces/cm^2, Ti and Mn if excessively present are not likely to involve anything adverse.

A certain method of analysis has previously been developed by the present invention so as to detect metallic contaminants introduced in single crystal silicon during the pulling stage by the Czochralski (CZ) method. This analysis method is conspicuously superior in accuracy to its conventional counterpart, as described in Japanese Patent Application No. 1-82840. Impurities, i.e. Cu, Fe, Ni, Cr, Ti and Mn, are determinable with the limits of detection in the order of 0.01×10^{-6} ppma; that is, a residual melt in a quartz crucible is examined at a solidification ratio of single crystal silicon grown in the CZ method in which polycrystalline silicon is molten with heat in the crucible, followed by immersion into the melt and pull of seed crystal therefrom and by subsequent continuous growth of single crystal rod. The invention is based upon the finding where correlations between the contents of individual impurities in single crystal pulled and the densities of OSF on the substrate processed therefrom were made clear by taking advantage of such high accuracy analysis.

Several publications disclose, only in part, that metal contamination causes OSF generation in single crystal silicon resulting from crystal growth by the pulling method, for example, Shimura, Tsuya and Kuwamura, J. Appl. Phys., Vol. 51, p.269 (1980) and F.G. Kirsht et al, Semiconductor Silicon 1986, edited by Huff, Abe and Kolbesen (Electrochemical Society, Boston, 1986), p.903. The silicon thus grown is known to lead to nucleation of minute defects due chiefly to the defects of lattice and to the presence of dissolved oxygen. This latter oxygen when in a super-saturated state develops minute defects and when carbon dissolved those defects increase over the level without dissolved carbon. It is to be recognized in the art that nucleation of minute defects will be caused also by metallic contaminants for reasons noted in connection with the behaviour of oxygen.

It has now been found that OSF densities can be selectively reduced to 100 pieces/cm^2 and to 10 pieces/cm^2 by the limitation of selected metals in specified concentrations and contents.

The invention will be further described by way of the following examples which should be construed as illustrative rather than restrictive.

Examples 1 to 6 and

Comparative Examples 1 to 4

Into a quartz crucible of 45 cm in diameter was charged 60 kg of polycrystalline silicon which was thereafter doped with phosphorus and molten with heat. An n-type, (100)-orientation, 15.5-cm diameter rod of single crystal silicon was pulled from the melt.

Impurity concentration in the single crystal silicon was quantitated by determining the concentrations of the various impurities in the crucible residue. The silicon melt was solidified, after pulling of the single crystal silicon, to the residue of about 100 g. The resulting residue melt was fully solidified by cooling, followed by comminution and cleaning on the surface and by subsequent dissolution in an aqueous mixture of hydrofluoric acid an nitric acid. Measurement of impurity concentrations was then made in accordance with ICP from which the concentrations of contaminants in the single crystal silicon were converted by the following equation.

$$C = C_0 \cdot k(1-X)^{k-1}$$

where

C   : impurity concentration in single crystal silicon,
C_0 : impurity concentration in initial charge,
k   : diffusion coefficient, and
X   : solidification ratio.

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As the parameter k, a value is used which is reported in W. Zulenhner et al, "Silicon Chemical Etching", Crystal, Vol 8, p.28. In general, heavy metal contaminants are extremely small in k, say about 10^{-6}, and hence likely to remain in almost all amounts in a residual melt without appreciable inclusion on silicon crystals. It is therefore sufficient to analyze the residual melt in determining the initial concentrations of contaminants as C_0. The ratio of solidification is zero at an initial stage. This is taken to mean that the foregoing equation may be rearranged to $C = C_0.k$. More specifically, the impurity concentration in single crystal silicon is defined as [impurity concentration in residual melt x silicon weight of residual melt (100 g)/crystalline silicon weight (60 kg)] x k.

The results obtained are shown in Table 1 along with the quantitative lower limits. Metals contained in the melt have been proved to be primarily Cu, Fe, Ni, Cr, Ti and Mn. Table 2 represents the quantitative lower limits of those six metals in single crystal silicon.

Table 1

Element	Concentration (ppma)	Lower limit (ppma)	Element	Concentration (ppma)	Lower limit (ppma)
Hf	<0.02	0.02	Mg	<0.01	0.01
Ta	<0.1	0.1	Al	2.0	0.01
W	<0.1	0.1	Ca	<0.1	0.1
Re	<0.1	0.1	Sc	<0.01	0.01
Os	<0.1	0.1	Ti	0.6	0.03
Ir	<0.07	0.07	V	<0.1	0.1
Pt	<0.03	0.03	Cr	4	0.002
Au	<0.03	0.03	Mn	1.5	0.001
Hg	<0.2	0.2	Fe	9	0.007
Tl	<0.3	0.3	Co	<0.01	0.01
Pb	<0.4	0.4	Ni	3.6	0.02
Bi	<0.3	0.3	Cu	0.5	0.03
Be	<0.03	0.03	Zn	<0.01	0.01
Ga	<0.03	0.03	Cd	<0.02	0.02
Ge	0.4		In	<0.08	0.08
As	<0.05	0.05	Sn	<0.4	0.4
Se	<0.5	0.5	Sb	<0.1	0.1
Sr	<0.01	0.01	Te	<0.3	0.3
Y	<0.003	0.003	Ba	<0.01	0.01
Zr	<0.01	0.01	La	<0.01	0.01
Nb	<0.1	0.1	Ce	<0.1	0.1

Table 1 (Cont'd)

Element	Concentration (ppma)	Lower limit (ppma)	Element	Concentration (ppma)	Lower limit (ppma)
Mo	<0.02	0.02	Pr	<0.1	0.1
Ru	<0.03	0.03	Nd	<0.03	0.03
Rh	<0.05	0.05	Sm	<0.05	0.05
Pd	<0.07	0.07	Eu	<0.01	0.01
Ag	<0.01	0.01	Gd	<0.03	0.03
Tb	<0.07	0.07	Tm	<0.05	0.05
Dy	<0.02	0.02	Yb	<0.02	0.02
Ho	<0.02	0.02	Lu	<0.01	0.01
Er	<0.02	0.02			

Table 2

Element	Lower limit $\times 10^{-6}$ (ppma)
Ti	0.0005
Cr	0.0001
Mn	0.00002
Fe	0.0001
Ni	0.001
Cu	0.02

Different single crystal silicon rods were prepared to have varied concentrations of the primary metals as shown in Table 3. On pulling at an overall length of 110 cm, each of the test silicon rods was sliced at an interval of 10 cm to wafers of 0.075 mm in thickness each for each. Mirror polishing, steam oxidation at 1,150 °C in a furnace, cooling to room temperature and removal of oxide film with aqueous hydrofluoric acid solution from the sample surface were done in that order. After etching by immersion into a selective etching solution for 2 minutes, the developed OSF density on the etched surface was examined on an optical microscope.

Cu, Fe, Ni and Cr when reduced to the specified contents prevent OSF development as evidenced by Table 3. Ti and Mo have turned out, even with increased contents, not to invite increased OSF.

Table 3

Impurity concentration x 10^{-6} (ppma)	Examples			
	1	2	3	4
Cu	0.1	0.05	0.05	0.05
Fe	0.05	0.12	0.05	0.05
Ni	0.05	0.05	0.06	0.05
Cr	0.05	0.05	0.05	0.1
Ti	0.3	0.3	0.3	0.3
Mn	0.2	0.2	0.2	0.2
OSF density (pieces/cm²)	80	50	75	50

Controls, comparative Examples 1 to 4, were prepared as shown in Table 4 and treated as in Examples 1 to 4.

Either one of Cu, Fe, Ni and Cr when exceeding the specified amounts reveals a sharp rise in OSF.

Table 4

Impurity concentration x 10^{-6} (ppma)	Comparative Examples			
	1	2	3	4
Cu	0.2	0.05	0.05	0.05
Fe	0.05	0.2	0.05	0.05
Ni	0.05	0.05	0.1	0.05
Cr	0.05	0.05	0.05	0.2
Ti	0.3	0.3	0.3	0.3
Mn	0.2	0.2	0.2	0.2
OSF density (pieces/cm²)	400	300	300	250

As has been confirmed from Table 5, Ti and Mn when set within the specified amounts, together with Cu, Fe, Ni and Cr, OSF is significantly reduced. This is particularly true of Example 6 in which all these metals are present at 0.05×10^{-6} ppma. OSF is nil.

Table 5

Impurity concentration (x 10^{-6} (ppma)	Examples	
	5	6
Cu	0.05	0.05
Fe	0.05	0.05
Ni	0.05	0.05
Cr	0.05	0.05
Ti	0.14	0.05
Mn	0.1	0.05
OSF density (pieces/cm²)	20	0

Claims

1. An n-type (100) oriented single crystal silicon for use as a substrate for semiconductor integrated circuits, which comprises as impurities Cu, Fe, Ni and Cr in an individual concentration of not more than 0.1×10^{-6} ppma and in a total concentration of not more than 0.4×10^{-6} ppma, whereby the silicon has not more than 100 oxygen-induced stacking faults per cm².

2. An n-type (100) oriented single crystal silicon for use as a substrate for semiconductor integrated circuits, which comprises as impurities Cu, Fe, Ni, Cr, Ti and Mn in an individual concentration of not more than 0.1 x 10⁻⁶ ppma and in a total concentration of not more than 0.6 x 10⁻⁶ ppma, whereby the silicon has not more than 10 oxygen-induced stacking faults per cm².

Patentansprüche

1. Einkristall-Silicium des n-Typs mit (100)-Orientierung zur Verwendung als Substrat für integrierte Halbleiter-Schaltungen, welches als Verunreinigungen Cu, Fe, Ni und Cr in einer Einzel-Konzentration von nicht mehr als 0,1 x 10⁻⁶ ppma und in einer Gesamtkonzentration von nicht mehr als 0,4 x 10⁻⁶ ppma umfaßt, wodurch das Silicium nicht mehr als 100 durch Sauerstoff induzierte Stapelfehler pro cm² aufweist.

2. Einkristall-Silicium des n-Typs mit (100)-Orientierung zur Verwendung als Substrat für integrierte Halbleiter-Schaltungen, welches als Verunreinigungen Cu, Fe, Ni, Cr, Ti und Mn in einer Einzel-Konzentration von nicht mehr als 0,1 x 10⁻⁶ ppma und in einer Gesamtkonzentration von nicht mehr als 0,6 x 10⁻⁶ ppma umfaßt, wodurch das Silicium nicht mehr als 10 durch Sauerstoff induzierte Stapelfehler pro cm² aufweist.

Revendications

1. Monocristal de silicium orienté (100) de type n destiné à être utilisé comme substrat pour circuit intégré semi-conducteur qui comprend comme impuretés Cu, Fe, Ni et Cr en une concentration individuelle n'excédant pas 0,1 x 10⁻⁶ ppma avec une concentration totale n'excédant pas 0,4 x 10⁻⁶ ppma, caractérisé en ce que le silicium ne possède pas plus de 100 défauts d'empilement induits par l'oxygène par cm².

2. Monocristal de silicium orienté (100) de type n destiné à être utilisé comme substrat pour les circuits intégrés semi-conducteurs qui comprend comme impuretés Cu, Fe, Ni, Cr, Ti et Mn en une concentration individuelle n'excédant pas 0,1 x 10⁻⁶ ppma avec une concentration totale n'excédant pas 0,6 x 10⁻⁶ ppma, caractérisé en ce que le silicium ne possède pas plus de 10 défauts d'empilement induits par l'oxygène par cm².